Synthesis and Properties of 2,4-Dialkoxy-1,3-di-t-butylcyclodiphosph(III)-azanes

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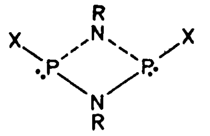
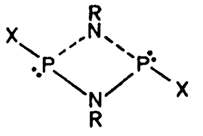
A series of alkoxycyclodiphosph(III)azanes, $XP(NBu^t)_2PY$ [X = Y = OMe (two isomers); X = Y = OEt (two isomers); X = Y = OCH_2CF_3 (one isomer); X = Y = OBu^t (one isomer); X = Cl, Y = OMe (one isomer)] has been prepared from the reactions of $ClP(NBu^t)_2PCl$ with alcohols in the presence of triethylamine. The product of reaction with Bu^tOH is easily converted into $(Bu^tO)P(NBu^t)_2P(O)H$. Analogous reactions with ethane-1,2- and propane-1,3-diols give the cage compounds $\overline{P(NBu^t)_2P{-}O(CH_2)_nO}$ (n = 2 or 3) and polymeric materials. Geometrical isomers of $(MeO)P(NBu^t)_2P(OMe)$ showed a different degree of reactivity towards methyl iodide, elemental sulphur, or selenium. Isomeric forms of the sulphides and selenides, $(MeO)P(NBu^t)_2P(X)(OMe)$ (X = S or Se), $(MeO)(X)P(NBu^t)_2P(X)(OMe)$ (X = S or Se), and of methyl iodide adducts have been obtained. Aspects of the ^1H, ^{13}C, and ^{31}P n.m.r. and i.r. spectra of cyclodiphosph(III)azanes are discussed.

THERE has recently been considerable interest in the synthesis of cyclodiphosph(III)azanes (1) [1-4] the chemistry of which is largely unexplored. Unexpectedly large differences in the properties of geometrical isomers of (1a) (*cis*) and (1b) (*trans*) have been found,[1-3] notably in their ^{31}P chemical shifts, and the relationship between (1) and the analogous phosph(III)azenes XP=NR, has been studied.[2,4-6] A series of alkoxy-derivatives (1; R = Ph, X = alkoxy) was recently reported,[7] and these results clarify earlier findings [8,9] as well as dispelling the impression that these derivatives might exist as phosph(III)azenes, XP=NPh.[10] We now report the synthesis of alkoxy-derivatives (1; R = Bu^t, X = alkoxy), the separation and comparison of the nucleophilic reactivity of geometrical isomers, and the formation of caged derivatives (1a) by reactions with diols.[11]



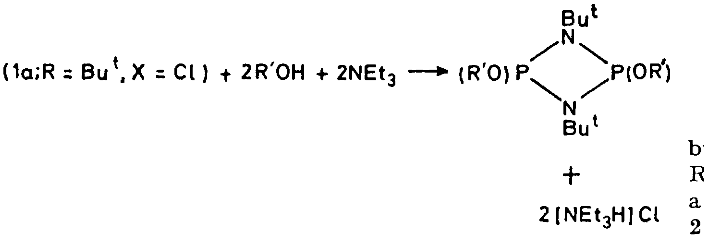
(1a)



(1b)

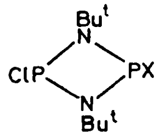
RESULTS

The reactions of (1a; R = Bu^t, X = Cl) with primary alcohols in the presence of triethylamine as hydrogen chloride acceptor gave 2,4-dialkoxycyclodiphosph(III)azanes in good yield:



R' = Me, Et, or CH_2CF_3

When R' = Me or Et, geometrical isomers with a difference in ^{31}P chemical shift of some 70 p.p.m. were obtained in roughly equimolar proportions. In the case where R' = CH_2CF_3, the yield of the isomer with the lower-field ^{31}P shift was relatively small and this isomer was not isolated, although the other isomer was readily obtained. In the former two cases the mixture of isomers was purified by vacuum distillation and the distillate contained an increased proportion of the isomer with the ' high-field ' ^{31}P shift (isomers are hereafter referred to as ' high-field ' or ' low-field ', depending on their ^{31}P chemical shift, see Table 1). On standing, both (1; R = Bu^t, X = Y = OMe or OEt) deposited crystals which on repeated recrystallisation from pentane gave the pure low-field isomers. Prolonged heating of the mixture of isomers gave almost pure samples of the high-field isomers. The monomethoxy-derivative (2; X = OMe) was obtained in good yield from an analogous reaction with 1 mol equivalent of methanol. Although a ready reaction with Bu^tOH was also apparent, the di-t-butoxy-derivative, (1a) or (1b) (R = Bu^t, X = OBu^t), could not be isolated in a pure state. On standing at ambient temperatures, or more rapidly by heating under reduced pressure, the product (3) of what is assumed to be butene elimination could be isolated. Reaction of (1a; R = Bu^t, X = Cl) with 1 mol equivalent of Bu^tOH gave a mixture of (2; X = OBu^t), (3), and starting material in a 2 : 1 : 1 ratio.



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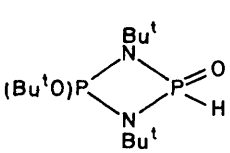

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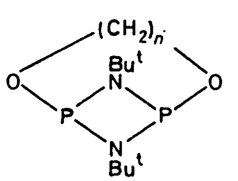
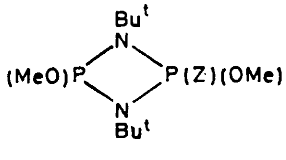


(4)

The reaction of (1a; R = Bu^t, X = Cl) with ethane-1,2- and propane-1,3-diols in the presence of triethylamine results in the formation of the new compounds (4; n = 2 or 3) which must have a mutual *cis* orientation of oxygen atoms.[11] N.m.r. spectroscopy showed that appreciable amounts of other, presumably polymeric, materials were also formed. The ' polymeric materials ' were less volatile than compounds (4), which could be separated from the former by distillation or sublimation under reduced pressure. Unfortunately, yields of (4) were reduced by heating during purification.

Compounds (1a) and (1b) (R = Bu^t, X = OMe) were also characterised by reactions with elemental sulphur and with selenium. These reactions were essentially stereospecific, so that each isomeric form [(1a) or (1b) (R = Bu^t, X = OMe)] gave an isomerically pure mono- (5) or di-oxidation (6) product which could finally be purified by distillation (5) or recrystallisation (6). No tellurides could be isolated, even from extended reactions with elemental tellurium. Reactions of (1a) or (1b) (R = Bu^t, X = OMe) with methyl iodide did not give the quaternary salts (5; Z = MeI) and (6; Z = MeI), but the corresponding Arbuzov-rearranged mono- and di-methylphosphonates (7) and (8), the latter only being formed after extended reaction periods. The same products, (7) and (8), could also be produced under more forcing conditions by heating (1a; R = Bu^t, X = OMe) *in vacuo* at 130 °C. Reaction of a 1 : 1 mixture of (1a) and (1b) (R = Bu^t, X = OMe) (total 2 mol equivalents) with sulphur, selenium, or methyl iodide (1 mol equivalent in each case) showed that the low-field isomer was always more reactive than the high-field isomer because the mono-oxidation product of the former was formed almost exclusively in each case. There appeared to be little or no difference between the rates of oxidation of isomeric forms of (5) or (7).



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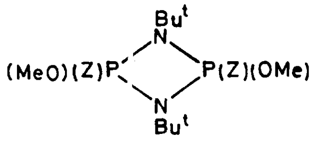

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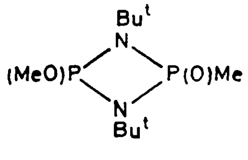

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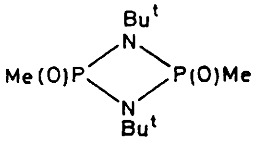

(8)

DISCUSSION

(*a*) *Structural Assignments*.—The formation of cyclophosph(III)azanes, rather than phosph(III)azene monomers, is clearly established by the n.m.r. data, where the ^1H and ^{13}C signals from the bridging *N*-butyl group in (1a) and (1b) generally showed triplet structure because of equal coupling to two phosphorus nuclei (Tables 1 and 2). Mass-spectral and chemical-reactivity data, for example in the formation of mono-oxidation products, clearly establish that four-membered rings are present. Although monomeric phosph(III)azenes of the type (R^1R^2N)P=NR^3 (R^1, R^2, and R^3 include Pr^i, Bu^t, and SiMe$_3$) have been isolated [2,4,6] and are characterised by particularly low-field ^{31}P shifts (generally > +300 p.p.m.), there was no ^{31}P n.m.r. evidence for phosph(III)-azenes, (RO)P=NBu^t, even with the tentatively identified compound (1a; R = Bu^t, X = OBu^t) which underwent loss of isobutene at ambient temperatures leaving (3). Analogous reactions have been observed for acyclic t-butyl phosphites.[12]

The reactions of (1a; R = Bu^t, X = Cl) and of (1a) or (1b) (R = Ph, X = Cl) [7] with alcohols are closely related. Both result in a ' low-field ' isomer, which on standing reverts to the thermodynamically favoured ' high-field ' isomer. These results are in marked contrast to the stability observed for (1a) and (1b) (R = Ph, X = dialkylamino) [1,13] and (R = SiMe$_3$, X = dialkylamino),[3] where it is the low-field isomer that is thermodynamically favoured. There is now a considerable body of evidence that the low-field isomers of the amino-derivatives, (1a) and (1b) [R = alkyl or SiMe$_3$; X = dialkylamino or N(SiMe$_3$)$_2$], have *trans* structures (1b).[2-4,14] By contrast in the alkoxy-derivatives (1a) and (1b) (R = Ph, X = alkoxy) it is the *cis* isomer that has a low-field ^{31}P signal.[7,15] It was therefore of interest to establish how this relates to the compounds reported here.

It was hoped that the synthesis of the caged derivatives (4) with *cis* structures would give a clear indication of the ^{31}P chemical shift to be expected for a *cis* isomer.[11] Compound (4; *n* = 2) has a ^{31}P chemical shift intermediate between that of the isomeric forms of (1; R = Bu^t, X = OMe or OEt), but the analogous trimethylene compound (4; *n* = 3) has a shift very close to those of the high-field isomers. At best these results suggest that the high-field isomers have *cis* structures, but the result is far from conclusive. The low-field ^{31}P shifts observed for the cyclodiphosph(III)azanes are well outside the range normally observed for analogous acyclic compounds [for example P(NMe$_2$)$_2$(OEt) has δ(P) + 135.7] [16] and the difference in shift between (4; *n* = 2) and (4; *n* = 3) indicates a conformational dependence on the phosphorus substituents. Molecular models indicate that non-eclipsed conformations can only be adopted by the methylene groups when the bridge adopts a twisted shape with respect to the P_2N_2 ring.

In the case of (1a) and (1b) (R = Bu^t, X = OMe), the dipole moments of the two isomers were measured, the high- and low-field isomers having moments of 2.1 and 1.5 D respectively in benzene solution.* This again tentatively suggests that the thermodynamically favoured high-field isomer has a *cis* structure.

The i.r. and Raman spectra of the isomeric forms of (1; R = Bu^t, X = OMe) were examined in order to establish which isomer has a centre of symmetry, but the results were ambiguous. There appeared to be more coincidences (within ±3 cm^{-1}) between the i.r. and Raman bands in the high-field isomer. Selected i.r. data are given in Table 3 and these show that the

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* Throughout this paper: 1 D ≈ 3.34 × 10^{-30} C m; 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Hydrogen-1 and ^{31}P n.m.r. data[a]

Compound (structure)	M.p. (θ_c/°C) or b.p. (θ_c/°C, P/mmHg)	δ(P)	$\lvert ^2J(PP)\rvert$	$\delta(OCH_n)$	$\lvert ^3J(POCH) + {}^5J(PNPOCH)\rvert$[b]	$\delta(CH_3)$	$\lvert ^2J(PCH) + {}^4J(PNPCH)\rvert$[c]	$\delta(CCH_3)$	$\lvert ^4J(PNCCH)\rvert$
$[(MeO)PNBu^t]_2$ (1a)	66, 0.1	133.7	*d*	3.48	10.1			1.29	<0.5
(1b)	56—60	202.4	*d*	3.65	9.0			1.24	0.7
$[(EtO)PNBu^t]_2$ (1a)	86—90, 0.1	131.4		3.92	7.6			1.29	<0.5
(1b)	50—55	209.7		3.98	7.0			1.24	0.8
$[(CF_3CH_2O)PNBu^t]_2$ (1a)	58—60, 0.04	143.3		4.17	6.5	δ(F) −75.5[e]	2.8[f]	1.30	<0.5
(1b)		222.9		4.23	*ca.* 6.5	δ(F) −74.6[e]	2.0[f]	1.23	0.9
$[(Bu^tO)PNBu^t]_2$ (1a)		129.6		1.45[g]	<0.4			1.34	0.4
$(MeO)P(NBu^t)_2PCl$ (2)	60—62, 0.03	188.0 (PCl) 137.8	*d*	3.75	8.1			1.38	0.8 (PCl) 0.6
$(Bu^tO)P(NBu^t)_2PCl$ (2)		191.8 (PCl) 163.8	49.7	1.46[g]	*h*			1.37	*h*
$\overline{CH_2OP(NBu^t)_2POCH_2}$ (4)	65—67	177.5	*i*	4.17	9.1			1.26	0.6
$\overline{CH_2CH_2OP(NBu^t)_2POCH_2}$ (4)	182	135.4		3.97	6.0			1.29	<0.3
$[(MeO)(S)PNBu^t]_2$ (6)	159—160	51.6		3.81	16.0			1.51	0.4
(6)	152—154	56.6		3.93	16.2			1.52	0.4
$(MeO)P(NBu^t)_2P(S)(OMe)$ (5)	54, 0.02	60.2 94.2	*j*	3.77 3.45	15.0 9.3			1.37	*ca.* 0.6 *ca.* 0.3
(5)	60, 0.03	75.7 110.0	*j*	3.71 3.59	15.5 8.7			1.35	*ca.* 0.5 0.9
$[(MeO)(Se)PNBu^t]_2$ (6)	141	46.4		3.78	16.8		954.5[k]	1.54	0.5
(6)	152—155	53.0		3.87	16.7		952.7[k]	1.55	0.5
$(MeO)(Se)P(NBu^t)_2P(OMe)$ (5)	34—36 72—76, 0.02	53.8 96.2	*j*	3.75 3.46	15.7 8.8		891.9[k]	1.39	*ca.* 0.4 <0.3
(5)	80, 0.07	72.3 119.3	*j*	3.73 3.65	16.0 8.6		893.5[k]	1.37	*ca.* 0.5 0.9
$[Me(O)PNBu^t]_2$ (8)	160	18.9				1.83	17.0	1.51	0.5
(8)	230—232	24.5				2.05	16.8	1.49	0.6
$Me(O)P(NBu^t)_2P(OMe)$ (7)	97—98	22.1 89.0	8.6 ±0.2	3.54	9.3	1.77	16.4	1.41	*ca.* 0.3 *ca.* 0.5
(7)	64, 0.05	38.0 131.4	<0.2	3.57	10.0	1.85	15.6	1.38	<0.3 *ca.* 0.5
$(Bu^tO)P(NBu^t)_2P(O)H$ (3)	114—116	−3.2 105.1	12.1 ±0.2	1.47[g]	1.1[l]	7.38[m]	590 ± 1[n] 2.4[o]	1.39	*ca.* 0.5 0.9
$(EtO)P(NBu^t)_2P(O)Me$ (9)		22.2 89.3	*h*	3.94	6.7	1.74	15.7	1.37	⩽0.5 ⩽0.5

[a] All data for $CDCl_3$ solutions; ^{31}P shifts are downfield (positive) from external 85% H_3PO_4, J values in Hz. [b] $^3J(POCH)$ in compounds of mixed oxidation state (±0.1 Hz). [c] $^2J(PCH)$ in compounds of mixed oxidation state (±0.1 Hz). [d] See ref. 21. [e] Fluorine-19 shifts are upfield (negative) from external CCl_3F. [f] $\lvert ^4J(POCCF)\rvert$ (±0.6 Hz). [g] $\delta(OBu^t)$. [h] Not measured. [i] Same sign as $\lvert ^3J(POCH) + {}^4J(POCCH) + {}^5J(PNPOCH)\rvert$. [j] See ref. 23. [k] $\lvert ^1J(PSe)\rvert$. [l] $\lvert ^4J(POCCH)\rvert$. [m] $\delta(PH)$. [n] $\lvert ^1J(PH)\rvert$. [o] $\lvert ^3J(PNPH)\rvert$.

TABLE 2

Carbon-13 n.m.r. data for cyclodiphosph(III)azanes[a]

Compound	M.p. (θ_c/°C) or b.p. (θ_c/°C, P/mmHg)	$\delta(C^1)$	$\lvert ^2J(PNC^1\rvert$	$\delta(C^2)$	$\lvert ^3J(PNCC^2\rvert$	$\delta(C^3)$	$\lvert ^2J(POC^3) + {}^4J(PNPOC^3)\rvert$
$[(MeO)PNBu^t]_2$ (1a)	66, 0.1	51.1	12.1	31.1	6.0	48.6	7.5
(1b)	56—60	50.9	6.0	30.2	5.4	48.1	2.9
$[(EtO)PNBu^t]_2$ (1a)	86—90, 0.1	51.2	12.5	31.1	6.1	57.5[b]	7.9
(1b)	50—55	51.0	6.1	30.5	5.5	56.9[c]	0
$[(CF_3CH_2O)PNBu^t]_2$ (1a)	58—60, 0.04	52.0	11.8	31.0	6.1	60.0[d]	8.3
$(MeO)P(NBu^t)_2PCl$ (2)	60—62, 0.03	52.9	9.8 (av)	30.7	5.7, 6.5	51.2	10.3[e]
$\overline{CH_2OP(NBu^t)_2POCH_2}$ (4)	65—67	51.1	10.5	30.3	5.7	66.8	4.5[f,g]
$\overline{CH_2CH_2OP(NBu^t)_2POCH_2}$ (4)	182	51.0	12.2	31.1	6.2	60.5[h]	8.4[g]
$(ClPNBu^t)_2$[i] (1a)	40—42	54.2	6.9	30.3	6.3		

[a] For $CDCl_3$ solutions at ambient temperature; ^{13}C shifts are downfield relative to internal $SiMe_4$. Coupling constants ±0.4 Hz. [b] $\delta(C^4)$ 17.2, $\lvert ^3J(POCC^4) + {}^5J(PNPOCC^4)\rvert$ 1.9 Hz. [c] $\delta(C^4)$ 16.4, $\lvert ^3J(POCC^4) + {}^5J(PNPOCC^4)\rvert$ 2.1 Hz. [d] $\lvert ^2J(FCC)\rvert$ 35.8 Hz; $\delta(C^4)$ 124.5, $\lvert ^3J(POCC^4) + {}^5J(PNPOCC^4)\rvert < 1.2$ Hz, $\lvert ^1J(FC)\rvert$ 277.3 Hz. [e] $\lvert ^2J(POC^3)\rvert$; $\lvert ^4J(PNPOC^3)\rvert$ 1.3 Hz. [f] Opposite sign to $^3J(POCH) + {}^5J(PNPOCH)$ as shown by ^{13}C-{^{1}H} experiments. [g] See text. [h] $\delta(C^4)$ 33.0, $\lvert J(POCC^4)\rvert$ 2.1 Hz. [i] Data from ref. 22.

TABLE 3

Selected i.r. data (cm^{-1}) [a]

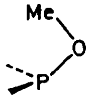
Compound	ν(P–O–C)	ν_{asym}(P–N–P) [b]	? [c]	ν(C–C)
(1; R = Bu^t, X = OMe) [d,e]	1 012, 1 030	897	704, 731	
(1; R = Bu^t, X = OMe) [f]	1 013, 1 030	890	699	
(1; R = Bu^t, X = OEt) [d,e]	1 029, 1 042	890	722, 738	930
(1; R = Bu^t, X = OEt) [f]	1 028	882	718	931
(1; R = Bu^t, X = OCH$_2$CF$_3$) [d,e]	1 020, 1 046	905	750, 784	960, 970
(2; X = OMe) [e]	1 015	892	731	
(4; n = 2) [f]	1 025, 1 048, 1 063	860	678	911
(4; n = 3) [f]	1 006, 1 021, 1 044	900		930, 940

[a] Strong absorptions in the range 650—1 050 cm^{-1}. [b] For (1; R = Bu^t, X = Cl), 905 cm^{-1}. [c] Strong bands, possibly ν_{sym}(P–N–P). [d] 'High-field,' thermodynamically favoured isomer. [e] Liquid films. [f] Nujol mulls.

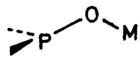
ring asymmetric stretching mode, ν_{asym}(P–N–P), is at higher energy in the high-field isomers. This band is at lower energy again in (4; n = 2), but close to that in the high-field isomers of (1; R = Bu^t, X = OMe or OEt) in (4; n = 3). The origin of the strong band(s) in the region 700—740 cm^{-1} is not established [although it may be ν_{sym}(P–N–P)]. The low-field isomers are characterised by one band in this region whereas the high-field isomers have two bands. Again the parallel between (4; n = 2), which has one strong band near this region (678 cm^{-1}), and the low-field isomers may be noted.

On balance, we favour the assignment that the thermodynamically favoured high-field isomers have *cis* structures. This is opposite to the assignment applied to the compounds (1a) and (1b) (R = Ph, X = alkoxy),[7] but an important factor here is the close parallel with the properties of the amino-compounds (1a) and (1b) (R = Bu^t, X = dialkylamino) where the same assignment is certain.[14,17] The marked tendency of cyclodiphosph(III)azanes to form *cis* structures in spite of adverse steric effects has yet to be explained. This is highlighted by the formation of small proportions of the low-field relative to the high-field isomers with (1a) and (1b) (R = OCH$_2$CF$_3$, X = Bu^t), and by the non-observation of a low-field isomer of (1a) and (1b) (R = OBu^t, X = Bu^t). On the other hand, bulky alkoxy-substituents may facilitate the isomerisation process. A definitive assignment must await a crystal-structure determination.

(*b*) *N.M.R. Parameters*.—It is anticipated that the preferred conformations of the exocyclic substituents will be reflected in the relative signs and magnitudes of the coupling constants $^2J(POC)$ [18] and $^3J(POCH)$.[19] In the absence of adverse steric effects the preferred conformation of an alkoxide group will be that in which the number of *gauche* interactions between non-bonded electrons on oxygen and phosphorus is maximised.[20] In the case of (1; R = Bu^t, X = OMe) this will be conformation (A) or (B), with a preference for (A). Conformation (A) was found in the crystal structure of (1b; R = Ph, X = OMe).[15] $^2J(POC)$ in particular should be small, possibly negative, in (A) and relatively large and positive in (B).[18] The ^{13}C n.m.r. spectra of (1a) and (1b) (R = Bu^t, X = alkoxy) generally consist of at least three triplets, those in the N–*C*–*C* region due to coupling to the two equivalent nuclei and those in the PO*C* region due to magnetic inequivalence of the ^{31}P nuclei. The spacing of the outer components of the latter 'triplet' is $|^2J(POC) + {}^4J(PNPOC)|$. Since $^4J(PNPOC)$ is small (1.3 Hz) in (2) this spacing is a close approximation to $^2J(POC)$. In the caged compounds (4; n = 2) and (4; n = 3) spin-coupling information may also be transmitted by the routes *P*–O–C–*C* and *P*–O–C–C–*C* respectively; deceptively simple proton 'triplets' could also be affected by coupling over *P*–O–C–C–*H* and *P*–O–C–C–C–*H* bonds respectively. In the following discussion, expressions for these couplings are not included, although their probable effects will be considered. Thus with (4; n = 2) a series of ^{13}C-{^{1}H} double-resonance experiments were used to demonstrate that $^2J(POC) + {}^4J(PNPOC)$ (4.5 Hz) is opposite in sign to $^3J(POCH) + {}^5J(PNPOCH)$ (9.1 Hz). The latter combination will be positive since four-[21] and five-bond couplings are small. Given that $^4J(PNPOC)$ is probably small (<2 Hz), and that the three-bond coupling is likely to be positive [it is 2.1 Hz in (4; n = 3)], then this compound appears to have the first known negative $P^{III}OC$ coupling (see ref. 18) although it cannot of course be measured accurately. There are striking differences in $^2J(POC) + {}^4J(PNPOC)$ when isomeric forms are compared (Table 2). This coupling is always larger in the *cis* isomer, and this is interpreted in terms of a greater population of a conformer analogous to (B), relative to (A), in the *cis* isomers. Conformer (B) would be favoured in the *cis* isomer because of the cross-ring steric interaction implicit in (A). The small negative coupling $^2J(POC) + {}^4J(PNPOC)$ in (4; n = 2) is consistent with this assignment, but the reason why the analogous coupling is 8.4 Hz in (4; n = 3) is not clear. This coupling has the same sign as $^3J(POCH) + {}^5J(PNPOCH)$ and is probably positive. Some support for these assignments was sought by comparisons of $^3J(POCH) + {}^5J(PNPOCH)$ obtained from the ^{1}H spectra (Table 1). This coupling is again smaller in the *trans* isomers, but the results obtained for (4; n = 2 or 3) do not indicate that the proton couplings have a marked stereochemical dependence (unless this coupling changes sign).



(A)

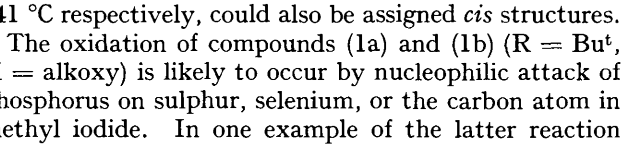


(B)

The coupling constants $^2J(PNC)$ (quaternary carbon) and $^4J(PNCCH)$ are dependent on the isomer examined and vary in the same way as for amino-derivatives.[17] Thus $^2J(PNC)$ is larger (>10 Hz) in the thermodynamically favoured *cis* isomers, relative to the *trans* isomers (<7 Hz). It is, therefore, surprising to find that $^2J(PNC)$ is only 6.9 Hz in (1a; R = Bu^t, X = Cl). $J(PNCCH)$ on the other hand is larger in the *trans* isomers, and is probably positive.[21] These couplings will vary with the dihedral angle between the phosphorus lone pair and the N–C bond [22] and will in part be dependent on the degree of ring puckering. It was recently found that $^2J(PNP)$, the sign and approximate magnitude of which can be obtained from ^{1}H-{^{31}P} INDOR measurements, is positive in *cis* isomers and negative in *trans* isomers of (1; R = Bu^t).[21] This is consistent with the positive couplings $^2J(PNP)$ found for (1; R = Bu^t, X = OEt) (high-field isomer) and for (4; *n* = 2). The sign of $^2J(PNP)$ in the mono- and di-oxidation products will be reported elsewhere.[23]

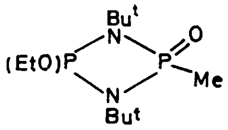
(*c*) *Oxidation Reactions*.—The reactions of (1a) and (1b) (R = Bu^t, X = OMe) with sulphur, selenium, and methyl iodide are particularly interesting in that the *trans* isomer (1b) was more readily oxidised than the *cis* (1a).

Spin couplings, ^1J(PSe),[24] in the range 890—960 Hz, and the methoxy-proton shifts, indicate that the =P(Se)(OMe) rather than the =P(O)(SeMe) group is present. The sulphides can be similarly formulated, *i.e.* =P(S)(OMe). However, on heating either of the isomeric forms of (6; Z = Se) with methyl iodide, sequential rearrangement of the =P(Se)(OMe) groups to =P(O)(SeMe) was observed [^1J(PSe) of the order of 500 Hz].[17] Both geometrical isomers of the mono-oxidation products were isolated and were not observed to interconvert, but there was no appreciable difference in the rate of formation of isomeric disulphides and diselenides from the mono-oxidation products. There is no direct evidence for the structures of these oxidation products, but the following reactions suggest that a *cis* isomer, (1a; R = Bu^t, X = OMe), gives mono- and di-oxidation products with a *cis* arrangement of methoxide groups:



We also note that the ^{31}P signals of *cis* isomers of $[(Me_2N)(X)PNBu^t]_2$ (X = S or Se) are upfield of the signals for the analogous *trans* isomers.[25] On this basis the disulphides and diselenides (6), m.p. 159—160 and 141 °C respectively, could also be assigned *cis* structures.

The oxidation of compounds (1a) and (1b) (R = Bu^t, X = alkoxy) is likely to occur by nucleophilic attack of phosphorus on sulphur, selenium, or the carbon atom in methyl iodide. In one example of the latter reaction it was established that the alkyl group bonded to phosphorus as a result of the Arbuzov rearrangement arises from the methyl iodide (and not the alkoxide group). Thus compounds (8) and (9) were the sole products of the reaction of methyl iodide with (1a; R = Bu^t, X = OEt), as identified by ^{1}H-{^{31}P} n.m.r. spectroscopy. The final step in the formation of an Arbuzov-rearranged product is unlikely to be rate-determining.[26] The thermodynamic instability of the *trans* isomers is therefore paralleled by their enhanced nucleophilic reactivity relative to the *cis* isomers. These differences would not appear to be steric in origin. This contention is supported by the fact that the lowest-energy bands in the photoelectron spectra of (1a) and (1b) (R = Bu^t, X = OMe) are *ca.* 0.5 eV lower in binding energy in the *trans* relative to the *cis* isomers.[14] These bands are likely to arise from an interaction between nitrogen and phosphorus lone-pair orbitals.[27] A thorough investigation into the bonding in geometrical isomers (1a) and (1b) will be needed to provide further insight into the reasons for the differences in their stability and reactivity.



(9)

EXPERIMENTAL

General experimental methods and spectroscopic techniques were as previously described.[1,28] Additionally, pulsed Fourier-transform ^{13}C n.m.r. spectra were obtained at 25.2 MHz on a Varian XL-100 n.m.r. spectrometer. Dipole moments were measured for solutions in benzene using a Marconi TF 2700 universal bridge and a variable condenser to measure capacitance.

The preparation of the isomers (1a) and (1b) (R = Bu^t, X = OMe) and their sulphides are described in detail below. The synthesis of the bicyclic compounds (4) has been described elsewhere.[11] Other preparative details and analytical data are given in Tables 4 and 5 respectively.

2-cis-4-*Dimethoxy- and* 2-trans-4-*Dimethoxy*-1,3-*di-t-butylcyclodiphosph*(III)*azanes* (1a) *and* (1b) (R = Bu^t, X = OMe).—Methanol (1.2 g, 37 mmol) and triethylamine (3.7 g, 36 mmol) were added dropwise to a stirred solution of 2-*cis*-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane (5.0 g, 18 mmol) in light petroleum (150 cm^3) (b.p. 40—60 °C) held at 0 °C. On completion of the addition, the mixture was boiled under reflux (0.5 h), the white precipitate removed, and solvent evaporated from the filtrate. The residual liquid was distilled under reduced pressure, b.p. 75—80 °C (0.2 mmHg), and left to stand (72 h) at ambient temperatures. During this time a crystalline solid was formed which was removed and recrystallised from pentane to give (1b; R = Bu^t, X = OMe) (0.9 g, 16%), m.p. 56—60 °C (Found: C, 45.0; H, 8.8; N, 10.4%; *m/e* 266. $C_{10}H_{24}N_2O_2P_2$ requires C, 45.1; H, 9.0; N, 10.5%; *m/e* 266). The oily product was heated at 100 °C (10 h) and redistilled to give (1a; R = Bu^t, X = OMe) (3.1 g, 64%),

TABLE 4

Experimental details

Substrate [amount/mmol]	Reactants [amount/mmol]	Reaction conditions [θ_c/°C, solvent (V/cm^3)]	Subsequent treatment [stirring (t/h) at θ_c/°C]; recrystallisation solvent	Final products (Yield/%) [isomer ratio]	M.p. (θ_c/°C) or [b.p. θ_c/°C, P/mmHg]
(1a; R = Bu^t, X = Cl) [20.0]	EtOH [40.0] NEt$_3$ [40.0]	20, light petroleum (b.p. 40—60 °C) (150)	as for (1; R = Bu^t, X = OMe)	(1a; R = Bu^t, X = OEt) (55) (1b; R = Bu^t, X = OEt) (20) [initially 1 : 2]	[86—90, 0.1] 56—60
[21.6]	CF$_3$CH$_2$OH [43.2] NEt$_3$ [43.2]	20, OEt$_2$ (150)	20 (1)	(1b; R = Bu^t, X = OCH$_2$CF$_3$) (65) [10 : 1]	[58—60, 0.04]
[16.7]	Bu^{t}OH [33.4] NEt$_3$ [33.4]	20, light petroleum (b.p. 60—80 °C) (120)	60 (3) light petroleum (b.p. 40—60 °C)	(1; R = Bu^t, X = OBu^t) (see Results) (3) (65)	114—116
[15.3]	MeOH [15.3] NEt$_3$ [16.0]	20, light petroleum (b.p. 40—60 °C) (100)	20 (0.5)	(2; X = OMe) (80)	[60—62, 0.03]
(1a; R = Bu^t, X = OMe) [9.15]	Se$_8$ [9.15]	20, C$_6$H$_6$ (10)	20 (1)	(5; Z = Se) (63)	34—36 [72—76, 0.02]
(1b; R = Bu^t, X = OMe) [4.42]	Se$_8$ [4.42]	20, C$_6$H$_6$ (10)	20 (1)	(5; Z = Se) (83)	[80, 0.07]
(1a; R = Bu^t, X = OMe) [11.4]	Se$_8$ [22.8]	20, C$_6$H$_6$ (15)	80 (4) light petroleum (b.p. 40—60 °C)–CH$_2$Cl$_2$ (10 : 1)	(6; Z = Se) (41)	141
(1b; R = Bu^t, X = OMe) [5.1]	Se$_8$ [10.2]	20, C$_6$H$_6$ (10)	80 (4) light petroleum (b.p. 40—60 °C)–CH$_2$Cl$_2$ (10 : 1)	(6; Z = Se) (61)	152—155
(1a; R = Bu^t, X = OMe) [4.48]	MeI [4.48]	20, CH$_2$Cl$_2$ (10)	20 (6), pentane	(7) (65) MeI (100)	97—98
(1b; R = Bu^t, X = OMe) [3.2]	MeI [3.2]	20, CH$_2$Cl$_2$ (5)	20 (0.5)	(7) (88) MeI (100)	[64, 0.05]
(1a; R = Bu^t, X = OMe) [8.5]	MeI [17.0]	20, C$_6$H$_6$ (10)	80 (24) light petroleum (b.p. 40—60 °C)–CH$_2$Cl$_2$ (1 : 1)	(8) (82) MeI (100)	160
(1b; R = Bu^t, X = OMe) [2.1]	MeI [4.2]	20, C$_6$H$_6$ (10)	80 (24) light petroleum (b.p. 40—60 °C)–CH$_2$Cl$_2$ (1 : 1)	(8) (78) MeI (100)	230—232
(1a; R = Bu^t, X = Cl) [18.7]	Bu^{t}OH [18.7] NEt$_3$ [18.7]	20, light petroleum (b.p. 40—60 °C) (150)	60 (2)	(2; X = OBu^t) (*ca.* 50) (3) (*ca.* 25) (1a; R = Bu^t, X = Cl) (*ca.* 25)	[82, 0.3]
(1a; R = Bu^t, X = OMe) [2.0]		Evacuated sealed tube	130 (16) light petroleum (b.p. 40—60 °C)–CH$_2$Cl$_2$ (1 : 1)	(8) (70)	160
(1a; R = Bu^t, X = OEt) [0.7]	MeI [0.7]	20, CDCl$_3$ (0.5)	20 (0.1)	(9) EtI	
(1b; R = Bu^t, X = OEt) [0.7]	MeI [1.4]	20, CDCl$_3$ (0.5)	90 (0.5)	(8) EtI	160
(1a; R = Bu^t, X = OMe) [0.309]	(6; Z = Se) (m.p. 141 °C) [0.309]	20, CDCl$_3$ (0.5)	20 (0.1)	(5; Z = Se)	34—36 [72—76, 0.02]
(1b; R = Bu^t, X = OMe) [0.231]	(6; Z = Se) (m.p. 152—155 °C) [0.231]	20, CDCl$_3$ (0.5)	20 (0.1)	(5; Z = Se) (5; Z = Se)	34—36 [72—76, 0.02] [80, 0.07]

TABLE 5

Analytical data

Compound [a]	X	Z	Found [b]				Calc.			
			C	H	N	m/e	C	H	N	m/e
(1a)	OEt		48.7_5	9.7_5	9.6	294	49.0	9.5	9.5	294
(1b)	OEt		49.1	9.8	10.0	294	49.0	9.5	9.5	294
(1a)	OCH$_2$CF$_3$		36.2	5.6	7.2	402	35.8	5.5	7.0	402
(2)	OMe		40.1	8.1	10.7	270 [c]	39.9	7.8	10.3_5	270
(4)	(n = 2)		45.2_5	8.5	10.5	264	45.4_5	8.3	10.6	264
(4)	(n = 3)		47.3	8.5_5	10.4	278	47.5	8.6	10.1	278
(6)		Se	28.6	5.8	6.4	426 [d]	28.3	5.7	6.6	426
(6)		Se	29.1	5.9	6.7	426 [d]	28.3	5.7	6.6	426
(5)		Se	35.1	7.4	8.3	346 [d]	34.8	7.0	8.1	346
(5)		Se	34.6	7.2	7.7	346 [d]	34.8	7.0	8.1	346
(8)			44.7	9.1	10.5	266	45.1	9.0	10.5	266
(8)			45.0	8.8	10.4	266	45.1	9.0	10.5	266
(7)			45.0	8.5	10.4	266	45.1	9.0	10.5	266
(7)			45.0	9.3	10.3	266	45.1	9.0	10.5	266
(3)			48.9	9.5	9.8	294	49.0	9.5	9.5	294

[a] Data for isomers are tabulated in the same order as in Table 1; for (1a) and (1b), R = Bu^t. [b] Analyses in %. [c] For ^{35}Cl-containing species. [d] For ^{80}Se-containing species.

b.p. 66 °C (0.1 mmHg) [lit.,[29] 66—68 °C (0.5 mmHg)] (Found: C, 45.1_5; H, 9.0; N, 10.5_5%; *m/e* 266). The yield of the *cis* isomer could be increased to *ca.* 80% by heating (24 h) the initial distillate at 120 °C.

2,4-*Dimethoxy*-1,3-*di-t-butyl*-2-*thioxocyclodiphosphazanes* (5).—Compound (1a; R = Bu^t, X = OMe) (1.84 g, 6.91 mmol) and sulphur (0.221 g, 6.91 mmol) were stirred (0.5 h) together in benzene (10 cm^3). The benzene was evaporated and the residue distilled under reduced pressure to give (5) (1.32 g, 64%), b.p. 54 °C (0.02 mmHg) (Found: C, 40.0; H, 8.3; N, 9.2%; *m/e* 298. $C_{10}H_{24}N_2O_2P_2S$ requires C, 40.3; H, 8.0_5; N, 9.4%; *m/e* 298). An isomer of (5) was obtained (88%) similarly, b.p. 60 °C (0.03 mmHg) (Found: C, 40.0; H, 8.0_5; N, 9.4%; *m/e* 298).

2,4-*Dimethoxy*-1,3-*di-t-butyl*-2,4-*dithioxocyclodi*-λ^5-*phosphazanes* (6).—Compound (1a; R = Bu^t, X = OMe) (1.04 g, 3.91 mmol) and sulphur (0.25 g., 7.82 mmol) were heated (6 h) together in toluene (6 cm^3) at 110 °C. The solvent was evaporated and the residue crystallised from light petroleum (b.p. 40—60 °C)–methylene chloride (3 : 1) to give (6) (0.96 g, 74%), m.p. 159—160 °C (lit.,[29] m.p. 124 °C) (Found: C, 36.2; H, 7.0; N, 8.6%; *m/e* 330. $C_{10}H_{24}N_2O_2P_2S_2$ requires C, 36.4; H, 7.3; N, 8.5%; *m/e* 330). A similar reaction with (1b; R = Bu^t, X = OMe) gave an isomer of (6) (56%), m.p. 152—154 °C (Found: C, 36.1; H, 7.4; N, 8.1%; *m/e* 330).

The relative rates of reaction of isomeric forms of (1; R = Bu^t, X = OMe) with sulphur, selenium, or methyl iodide (all in benzene solution) were measured as described above, monitoring the progress of the reaction by ^1H n.m.r. spectroscopy. $^1H\text{-}\{^{31}P\}$ experiments were also used to confirm the nature of the products. Reactions of isomers of (5; Z = S or Se) and (7) with sulphur, selenium, and methyl iodide respectively were also carried out on an n.m.r.-tube scale.

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REFERENCES

[1] G. Bulloch, R. Keat, and D. G. Thompson, *J.C.S. Dalton*, 1977, 99.
[2] O. J. Scherer and W. Glässel, *Chem. Ber.*, 1977, **110**, 3874.
[3] W. Zeiss, C. Feldt, J. Weis, and G. Dunkel, *Chem. Ber.*, 1978, **111**, 1180.
[4] E. Niecke, W. Flick, and S. Pohl, *Angew. Chem. Internat. Edn.*, 1976, **15**, 309.
[5] S. Pohl, *Z. Naturforsch.*, 1977, **B32**, 1344.
[6] E. Niecke and O. J. Scherer, *Nachr. Chem. Techn.*, 1975, **23**, 395.
[7] W. Zeiss and J. Weis, *Z. Naturforsch.*, 1977, **B32**, 485.
[8] A. Michaelis and G. Schroeter, *Chem. Ber.*, 1894, **27**, 490.
[9] T. Kawashima and N. Inamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 1924.
[10] O. Mitsunobu and T. Mukaiyama, *J. Org. Chem.*, 1964, **29**, 3005.
[11] R. Keat and D. G. Thompson, *Angew. Chem. Internat. Edn.*, 1977, **16**, 797.
[12] W. Gerrard and H. R. Hudson, *Org. Phosphorus Compounds*, 1973, **5**, 32.
[13] W. Zeiss, personal communication.
[14] R. Keat, A. N. Keith, A. MacPhee, K. W. Muir, and D. G. Thompson, *J.C.S. Chem. Comm.*, 1978, 372.
[15] W. Schwarz, H. Hess, and W. Zeiss, *Z. Naturforsch.*, 1978, **B33**, 723.
[16] D. Houalla, M. Sanchez, and R. Wolf, *Bull. Soc. chim. France*, 1965, 2368.
[17] R. Keat and D. G. Thompson, unpublished work.
[18] M. Haemers, R. Ottinger, D. Zimmerman, and J. Reisse, *Tetrahedron Letters*, 1973, 2241.
[19] G. Mavel, *Ann. Rev. N.M.R. Spectroscopy*, 1973, **B5**, 37.
[20] S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.
[21] R. Keat and D. G. Thompson, *J.C.S. Dalton*, 1978, 634.
[22] G. Bulloch, R. Keat, and D. S. Rycroft, *J.C.S. Dalton*, 1978, 764.
[23] G. Bulloch, R. Keat, D. S. Rycroft, and D. G. Thompson, unpublished work.
[24] C. Glidewell and E. J. Leslie, *J.C.S. Dalton*, 1977, 527.
[25] R. Keat, K. W. Muir, and D. G. Thompson, *Tetrahedron Letters*, 1977, 3087.
[26] A. J. Kirby and S. G. Warren, ' The Organic Chemistry of Phosphorus,' Elsevier, Amsterdam, 1967, p. 37.
[27] A. H. Cowley, D. W. Goodman, N. A. Kuebler, M. Sanchez, and J. G. Verkade, *Inorg. Chem.*, 1977, **16**, 854.
[28] G. Bulloch and R. Keat, *J.C.S. Dalton*, 1974, 2010.
[29] I. J. Colquhoun and W. McFarlane, *J.C.S. Dalton*, 1977, 1674.